Effect of silica nanoparticles on the phase inversion of liquid-liquid dispersions

Maliheh Raji Asadabadi*, Hossein Abolghasemi*,†, Mohammad Ghannadi Maragheh**, and Payman Davoodi Nasab*

*School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran
**Faculty of Nuclear Engineering and Physics, Amir Kabir University, Tehran, Iran

Abstract−The effect of silica nanoparticles on phase inversion of liquid-liquid dispersions in a stirred vessel was investigated. The studied systems were toluene dispersed in water and vice versa. In the first set of experiments, phase inversion behavior of systems without Silica nanoparticles was evaluated and subsequent experiments were conducted in the presence of the nanoparticles. For this purpose, Silica nanoparticles of different concentrations (0.01, 0.03, 0.05, 0.07 wt%) were dispersed in water. The nanofluid stability was examined using an ultraviolet-visible (UV-vis) spectrophotometer. The results indicated that increase in silica nanoparticle concentrations up to 0.07 wt% led to increase in agitation speed of phase inversion 43-53.5% and 38.5-45% in the case of O/W and W/O dispersions, respectively. Consequently, the tendency of dispersions to inversion diminished as nanoparticle concentrations increased. Finally, 0.05 wt% of silica nanoparticle was selected as the optimum on the range studied.

Key words: Phase Inversion, Dispersion, Nanoparticle, Agitation Speed, Holdup

INTRODUCTION

Liquid-liquid dispersions consist of two immiscible liquids. These systems, which are usually composed of an aqueous (water) and an organic (oil) phase, have various applications in many chemical processes in which contact between liquids is necessary to improve heat and mass transfer. For example, liquid-liquid extraction, multiphase reactions, direct heat transfer and preparation of emulsions in pharmaceutical and food industries are frequently encountered with two-phase liquid-liquid. Most of these dispersions are produced in agitated vessels, and depending on the conditions, one of the liquids (dispersed phase), which has lower volume fraction, forms droplets in the other one (continuous phase). There are two main kinds of dispersions: oil in water (O/W), which characterizes oil dispersed in water, and water in oil (W/O), which means water is the dispersed phase.

At steady state, there is a dynamic equilibrium between coalescence and breakup rate of dispersed drops. Large holdups and high degree of power input are often applied to many industrial processes in order to achieve high efficiency and productivity. Such operations may lead to the deviation from the steady condition at a critical value, if the limitations of these changes are not considered. Hence, the coalescence rate of drops increases and transcends the breakage rate, which results in a spontaneous event called phase inversion [1-7]. This phenomenon was reported by Rodger et al. [8] for the first time and refers to the conversion between two types of dispersions. For example, an O/W dispersion inverts to a W/O dispersion and vice versa. The phase inversion point is defined as the dispersed phase holdup beyond which is replaced by the continuous phase. The "ambivalent region" is a range of volume fractions in which either phase can be continuous and it is attributed to

the hysteresis effect of phase inversion between oil and water continuous dispersions [2,6,9-11].

It has been found that this phenomenon is coupled with a maximum in the viscosity of dispersion and the formation of a number of secondary and multi dispersions by using laser induced fluorescence (LIF) technique [12]. It has also been observed that it is a time-dependent process and the phase inversion delay time depends on variety of parameters [13].

The variation of a dispersion morphology due to the phase inversion results in a system with entirely different properties such as drop size of dispersed phase, rheological characteristics, settling time, interfacial area, pressure drop value in pipelines and rate of heat exchange, mass transfer and chemical reaction, as well [2,11,13].

Phase inversion can be regarded as a troublesome event in some chemical processes and can affect the performance of systems. For instance, it must be prohibited in liquid-liquid extraction equipment such as mixer-settlers. On the other hand, some industrial processes take advantage of it. For example, it is a convenient technique to achieve the favorite fine emulsions by consuming lower surfactant concentration and energy input compared with direct emulsification method, particularly in the case of viscous fluids and polymers in food, paint and cosmetic manufacturing industry [14-16]. In addition, phase inversion can be utilized in process intensification because it has been revealed that higher mass transfer was obtained in the vicinity of phase inversion [17].

Hence, it is crucial to determine the phase inversion point for the design of chemical engineering systems such as mixer-settlers, pumps and pipelines or in order to produce desirable dispersion. As a result, it has been an intensively studied topic for many investigators. Various empirical correlations and some theoretical models have been proposed for estimating the phase inversion point based on several supposed physical mechanisms [18-22]. Juswandi [19] presented a stochastic model to simulate phase inversion via the Monte Carlo technique and applied the minimization of the total energy content

†To whom correspondence should be addressed.
E-mail: hoab@ut.ac.ir

in the system as a rational criterion for determination of the phase inversion volume fraction. Subsequent authors developed it by incorporating the hydrodynamics of drop coalescence and breakup into a model [21] and modeled the hysteresis that is along with phase inversion [20].

According several investigations in the literature, some parameters which principally influence the inversion point are:

• Physical and physico-chemical properties of the continuous and dispersed phase such as density, interfacial tension and viscosity that is the most significant one [4,5,10,13,18,22].

• Operating parameters such as impeller agitation speed, and location, type, number and size of the impellers [4,10]. Even so, Deshpande and Kumar [1] proposed that the inversion holdup will be independent of operational variables at high intensity of turbulence as Selker and Sleicher [10] and Lunning and Sawistowski [18] had reported.

• Wetting characteristics and substance of the equipment involved in the process [13,23].

• Applying an electric field [24].

• Mass transfer and presence of the other components in the liquid-liquid systems such as salts and surfactants [25].

Surfactant (emulsifier) is a third component introduced into emulsions to render them kinetically stable. Surfactants reduce the interfacial tension by adsorption at the interface and retarding the drainage of the continuous film between two drops of dispersed phase, and therefore result in the decline of coalescence rate [26]. Thus, they can change inversion behavior of emulsions.

Nanoparticles have attracted considerable interest due to their great features and applications. It is now well known that colloidal solid particles can be used to promote the stability of emulsions instead of surfactants, owing to some of their advantages such as lower cost and toxicity over the surfactants [27,28]. The mechanism of stabilization of this so-called "Pickering emulsion" has been broadly studied, and it was expressed that particles can strongly adsorb at the interfaces and prevent the coalescence by steric hindrance or formation of a 3-D network of particles between droplets [29-32]. Therefore, nanoparticles affect the inversion process of emulsions but not similar to the surfactants. Meanwhile, important factors controlling their performance are wettability, concentration [33], size, shape, and location of the particles. In the published papers concerning the stabilization of emulsion with fine solid particles [34-37], the ability of solid particles for preparing stable emulsions against creaming, coalescence, and Ostwald ripening was often evaluated. For this purpose, after stopping mechanical agitation, the stability of emulsions was assessed by measuring the volume of the produced emulsions and percentage of oil released after a given time. In fact, the criterion for the stability of emulsion was time of phase separation and breakdown of emulsions, but in the current work we focused on the phase inversion phenomenon as a criterion for assessment of the stability of toluene-water dispersions (temporary emulsions).

Inversion of Pickering emulsions is often achieved via varying the hydrophile-lipophile balance of solid particles [30], for example, by changing the particle concentration [33], using mixture of two particle type with different wettability [38] (transitional inversion) or altering the volume fraction of dispersed phase of emulsions (catastrophic inversion) at a fixed amount of nanoparticles

[32].

We studied the effect of presence of low concentrations of silica nanoparticles (compared with other researches) on catastrophic phase inversion of systems containing different content of these nanoparticles. In addition, stability of nanofluids was examined.

The catastrophic phase inversion point at different holdups of the dispersed phase was achieved through changing the energy input in liquid-liquid systems with or without nanoparticles. Therefore, the phase inversion point corresponds to the agitation speed at which dispersed phase turns into the continuous phase.

EXPERIMENTAL

1. Materials

The liquid-liquid system under investigation consists of deionized water, toluene and silica nanoparticle. Distilled water (PH~7) having a density of 996 Kg/m^3 and a viscosity of 0.96 mPa·s was used as the aqueous phase and toluene (purity>99%, product of Merck Co.) having a density of 870 Kg/m^3 and a viscosity of 0.57 mPa·s was the organic phase. Silica nanoparticles with a BET surface area of 200 m^2/g and average primary particle size of 12 nm were supplied by Degussa (Aerosil R200).

The interfacial tension of the toluene-water system is 0.036 N/m, as measured by a Kruss digital tensiometer K10T (Hamburg, Germany). Fig. 1 demonstrates interfacial tension of the system versus the several concentrations of the silica nanoparticles in the system.
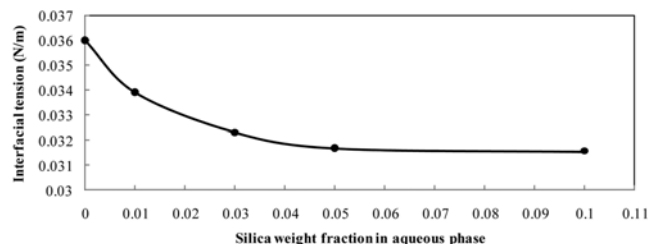

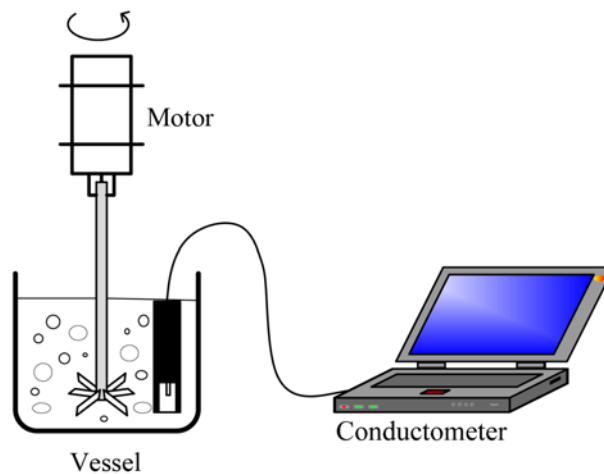**Fig. 1. Interfacial tension for different concentrations of SiO$_2$ nanoparticles.**

Fig. 2. Schematic diagram of the apparatus used for the phase inversion experiments.

2. Apparatus

The experimental setup, presented in Fig. 2 consists of:

i) A non-baffled glass vessel with internal diameter (D_T) and height of (H) 8.5 cm and 12.5 cm, respectively.

ii) A six pitched blade turbine impeller of 4 cm in diameter (d/D_T=0.47) connected to a cylindrical shaft for mixing the phases and both of them were made from stainless steel. The impeller was located in the center of the vessel at 1/3 height of the vessel based on the design rules of mixing equipment.

iii) A variable speed stirring motor to drive the impeller which is equipped with a digital tachometer to adjust the agitation rate in the range of 0-2,000 rpm.

The conductivity of dispersions was measured using a micro-processor-pocket-conductivity meter (model LF96) to identify the phase inversion point. In addition, it could act as a baffle for the system.

3. Procedure

All the experiments were carried out at room temperature. Prior to each run, the liquids were mutually saturated with each other to prevent mass transfer between them and the equipment was cleaned by acetone and tap water to ensure the absence of any contamination, which affect the phase inversion process.

To study the impact of silica nanoparticles on the phase inver-

sion point in toluene-water system, ten sets of experiments were performed by varying the nanoparticle concentrations (0, 0.01, 0.03, 0.05, 0.07 wt%) at different holdups. For preparing silica nanoparticle dispersion in water, in every experiment a specified amount of silica powder was added to the saturated water as a base fluid and then ultrasonicated for 1 h (Misonix sonicator 3,000, 500 W, 20 KHz). Morphological characteristics of Silica nanoparticles are shown in Fig. 3(a) and (b). In this figure, the scanning electron microscope (SEM) image illustrates the spherical morphology of nanoparticles, and dynamic light scattering (DLS) shows the presence of particles between 16-83 nm with a mean diameter of 37 nm in the dispersion.

In the first step of phase inversion experiments, certain volumes of the aqueous and organic phase were introduced to the vessel to set a proper holdup at a chosen concentration of the nanoparticles. Meanwhile, according to which phase is dispersed phase, holdup was determined by the equation below:

$$\varphi_d = \frac{V_d}{V_d + V_c} \tag{1}$$

Where V_c and V_d are the continuous and dispersed phase volume and φ_d is the favorable hold up.

For the formation of primary dispersions, a minimum agitation speed was applied and after that, the agitation speed increased gradually at constant holdup in the case of O/W dispersions until phase inversion occurred. To make sure of accurate determination of the agitation speed of inversion point, the experiments were repeated at least three times and near the inversion point, impeller speed altered precisely. In the case of W/O dispersions the same procedure was repeated, but differed in that phase inversion point was obtained by gradually decreasing the agitated speed.

4. Conductivity Measurements

Four techniques have been proposed to specify the phase inversion point, including optical assessment, monitoring the viscosity, analysis of the electrical resistance, and measuring the conductivity of the dispersions [28]. In this study, phase inversion was detected visually and by successively measuring the conductivity of the dispersions as the conductivity of the water and oil continuous dispersions differ by several orders of magnitude. Fig. 4 illustrates an example of the change in dispersion conductivity with variation of the agitation speed of impeller, and a sharp shift in conductivity is observed at the phase inversion point.

RESULT AND DISCUSSION

Fig. 5 depicts the phase inversion map for O/W and W/O disper-
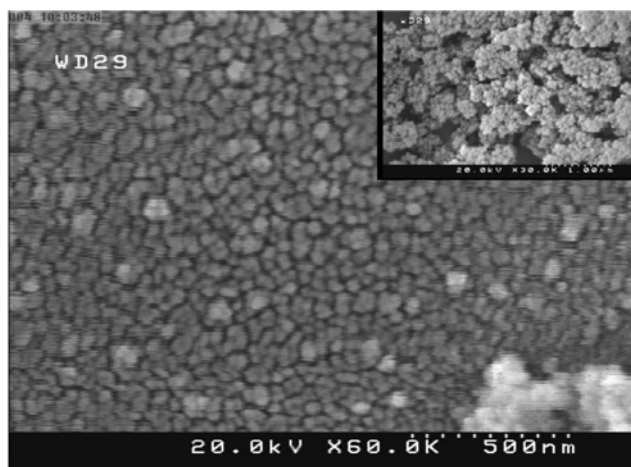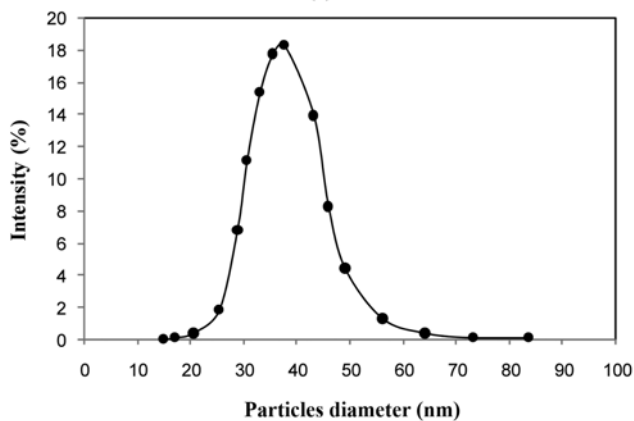
Fig. 3. (a) SEM image of Silica nanoparticles. (b) Size distribution of Silica nanoparticles dispersed in water.
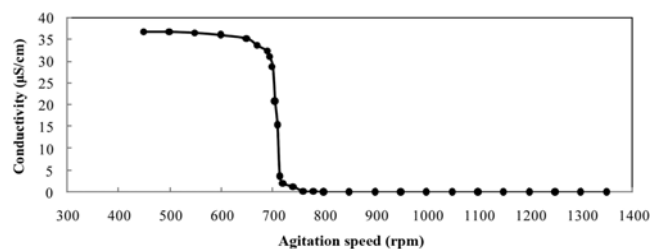

Fig. 4. Conductivity of toluene-water system as a function of the agitation speed.
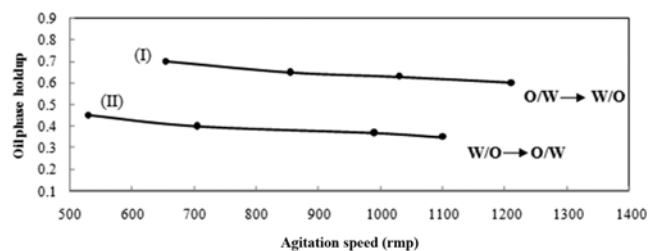
Fig. 5. Phase inversion characteristics for toluene-water system in the absence of nanoparticles.

sions of toluene-water system without silica nanoparticles. In this figure, the organic phase volume fraction against the agitation speed is plotted. The upside curve (I) exhibits the phase inversion from O/W to W/O dispersions induced by increasing the agitation speed, and the underside curve (II) shows the phase inversion from W/O to O/W dispersions caused by decreasing the agitation speed. As mentioned before, there is an ambivalent region between these two curves where both types of dispersions can be formed depending on the conditions.

The experimental results indicate that the energy input required for the O/WW/O inversion (curve (I)) increases while the dispersed phase holdup decreases. As a result, it can be claimed that O/W dispersions with lower volume fraction of toluene need more power input of mixing in order to invert to W/O dispersions and they are more stable. This trend is contrary to the W/O→O/W inversion (curve (II)) in such a manner that the agitation speed of phase inversion decreases as the volume fraction of water decreases, so the stability of the W/O dispersion reduces. This reverse behavior for O/W and W/O dispersions is in line with the results of the previous investigators who studied the phase inversion behavior of different continuous and semi-batch systems by gradually increasing the amount of disperse phase instead of changing the agitation intensity used in this work. It was found that this trend is due to the some differences in the structures of water and oil continuous dispersions [3,4,11,22].

Fig. 6 illustrates the effect of the silica nanoparticles concentration on the phase inversion locus of toluene-water system at different holdups. The upper and lower curves of ambivalent region for each certain concentration of nanoparticles show similar trends of the systems without nanoparticles. As can be seen, adding silica nanoparticles into the system causes both curves to shift consistently to the right. These behaviors suggest that the presence of nanoparticles alters the physical properties of this liquid-liquid system. According to Einstein's formula for determination of nanofluid vis-
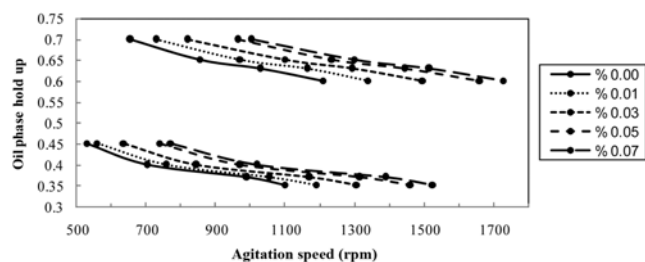

Fig. 6. Effect of Silica nanoparticle concentrations on the phase inversion point of toluene-water system.

cosity [39], the viscosity change of the aqueous phase was not considerable by adding nanoparticles and could not greatly affect the ambivalence behavior. On the other hand, existence of nanoparticles could reduce the interfacial tension, which has an influential effect on the ambivalent range. Although this reduction is not large compared to the surfactants, it cannot be disregarded (Fig. 2).

As it was noted previously, nanoparticles can play the role of emulsifiers because colloidal particles provide steric hindrance between drops of the dispersed phase and make their coalescence more difficult. Hence, silica nanoparticles enhance the stability of the system, and consequently phase inversion occurs at higher agitation speed for O/W and W/O dispersions. To reach the phase inversion point, for an O/W dispersion containing nanoparticles, more stirring energy at fixed holdup is needed in comparison to O/W dispersions having no nanoparticles as shown in Fig. 6. In the case of W/O dispersions similar results are observed, revealing that in the presence of silica nanoparticles the tendency to the inversion diminishes, and therefore higher energy input at constant holdup is required for phase inversion to occur. The results also show that the effect of nanoparticles is more pronounced for O/W dispersions since the silica nanoparticles are hydrophilic and they are often used to stabilize O/W emulsion (permanent dispersions). From the other point of view, these nanoparticles can also affect the phase inversion behavior of W/O dispersions, which is ascribed to the decline in interfacial tension of toluene-water system. These observations are in agreement with earlier studies concerning phase inversion, which reported that lower interfacial tension caused phase inversion to happen at higher volume fraction of the drop phase under a constant agitation speed [4].

Based upon Fig. 6, using more amounts of silica nanoparticles moves both curves towards upper agitation speed and expands the stability range of dispersions that is favorable for processes which high agitation speed is needed. As shown in this figure, an increase in silica nanoparticle concentrations from 0 to 0.07 wt% leads to 500 rpm average rise in agitation speed of phase inversion. The highest agitation speeds of phase inversion correspond to O/W and W/O dispersions containing 0.07 wt% of silica nanoparticles at dispersed phase volume fraction of 0.6 and 0.65 which are 1,730 rpm and 1,525 rpm, respectively. However, we found that 0.05 wt% is the optimum concentration of silica nanoparticle in the range explored in our experiments because further increase up to 0.07 wt% increases the agitation speed of phase inversion almost 58 rpm. This increase compared with the enhancement rate of lower concentrations is not considerable. This fact suggests that higher concentrations than 0.05 wt% of silica nanoparticles have little influence on phase inversion and make no significant difference. This trend may be attributed to the minimum interfacial tension, which corresponds to 0.05 wt%. Furthermore, by using more nanoparticles the risk of particle sedimentation and agglomeration increases and that prevents some particles adsorbing at the interface.

1. Analysis of Nanofluid Stability

Since the stability of aqueous nanofluids affects the performance of nanoparticles and consequently phase inversion behavior of the system, the stability of nanofluids was investigated by using a UV-visible spectrophotometer (Cintra 6, GBC Scientific equipment Ltd., Australia).

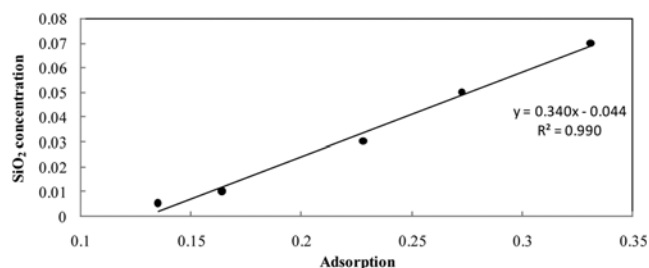Absorbency of each nanofluid at the wavelength of 320 nm (cor-

Fig. 7. Calibration curve of silica concentration with corresponding light absorption.
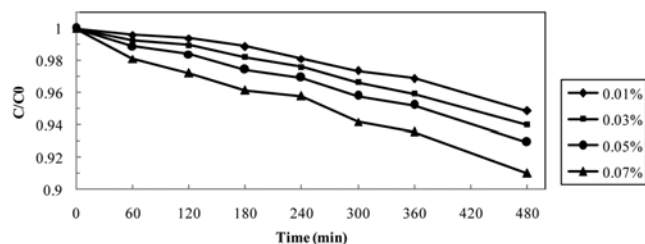

Fig. 8. Variation in relative concentration of silica in nanofluids over time.

responding to peak absorbance) was measured at regular intervals. The concentration of suspended particles in the suspension is proportional to the absorbency of nanofluids and a linear relation between them is presented in Fig. 7. Therefore, lower change in absorbency means lower degree of concentration variation of suspended nanoparticles or better stability of nanofluids for a given period.

Fig. 8 illustrates the colloidal stability of nanofluids with different initial concentration of silica nanoparticles. The relative concentration (C/C_0) of silica nanoparticles at different initial concentrations decreases with time and nanofluid stability decreases as the concentrations increase. Owing to this figure, it can be asserted that all of the nanofluids show good stability during the phase inversion experiments.

CONCLUSIONS

We investigated the effect of presence and concentration of silica nanoparticle on the phase inversion of toluene-water system. The major results of this study are as follows. An increase in silica nanoparticle concentration from 0 to 0.07 wt% reduces interfacial tension of the system about 12.5%, improves the stability range of dispersions, and causes phase inversion to occur at higher agitation speeds. These speed enhancements are 43-53.5% and 38.5-45% for O/W and W/O dispersions compared with pure systems, respectively. Findings confirm that nanoparticles are able to stabilize dispersions, so prevention of the phase inversion even at high agitation speeds is possible by applying appropriate amount of them in dispersions for industrial applications. Results show that the minimum value of interfacial tension is achieved at 0.05 wt% of silica and the effect of higher concentrations on the interfacial tension is negligible. At 0.05 wt% of silica nanoparticle, the agitation speed of phase inversion increases from 190 up to 430 rpm at different holdups of the dispersed phase with respect to the systems without nanoparticles. Indeed, at this concentration the variation rate in agitation speed

of phase inversion is greater than at higher concentration.

Based on our work, using 0.07 wt% silica nanoparticle gives rise to the highest agitation speed, i.e., the widest range of dispersion stability, but we found that 0.05 wt% is the optimum and most efficient concentration in our system and experimental conditions according to above mentioned reasons. In addition, the results of nanofluid stability indicate that the relative concentration of 0.05 wt% silica nanofluids decreases about 1.6% 1 h after preparation. For 0.07 wt% silica nanofluids, it is about 2.7%. Hence, 0.05 wt% Silica nanofluids are more stable against sedimentation.

NOMENCLATURE

C   : concentration of nanoparticles suspended in base fluid [kg/m^3]
C_0 : initial concentration of nanoparticles in base fluid [kg/m^3]
V_c : continuous volume [m^3]
V_d : dispersed phase volume [m^3]

Greek Letters
φ_d : dispersed phase hold-up

REFERENCES

1. B. Deshpande and S. Kumar, *Chem. Eng. Sci.*, **58**, 3829 (2003).
2. K. Ioannou, O. J. Nydal and P. Angeli, *Exp. Therm. Fluid Sci.*, **29**, 331 (2005).
3. S. Kumar, *Chem. Eng. Sci.*, **51**, 831 (1996).
4. M. A. Norato, C. Tsouris and L. L. Tavlarides, *Can. J. Chem. Eng.*, **76**, 486 (1998).
5. A. W. Nienow, *Adv. Colloid Interface Sci.*, **108-109**, 95 (2004).
6. F. Groeneweg, W. G. M. Agterof, P. Jaeger, J. J. M. Janssen, J. A. Wieringa and J. K. Klahn, *Trans. IChemE (PartA)*, **76**, 55 (1998).
7. J. K. Klahn, J. J. M. Janssen, G. E. J. Vaessen, R. de Swart and W. G. M. Agterof, *Colloids Surf. A- Physicochem. Eng. Asp.*, **210**, 167 (2002).
8. W. A. Rodger, V. G. Trice Jr. and J. H. Rushton, *Chem. Eng. Prog.*, **52**(12), 515 (1956).
9. J. Hapanowicz, *Flow Meas. Instrum.*, **21**, 284 (2010).
10. A. H. Selker and C. A. Sleicher Jr., *Can. J. Chem. Eng.*, **43**, 298 (1965).
11. R. N. Reeve and J. C. Godfrey, *Trans. IChemE (PartA)*, **80**, 864 (2002).
12. L. Liu, O. K. Matar, E. S. Perez de Ortiz and G. F. Hewitt, *Chem. Eng. Sci.*, **60**, 85 (2005).
13. T. R. Guilinger, A. K. Grislingas and O. Erga, *Ind. Eng. Chem. Res.*, **27**, 978 (1988).
14. L. A. Roberts, F. Xie and B. W. Brooks, *Colloids Surf. A- Physicochem. Eng. Asp.*, **274**, 179 (2006).
15. S. Sajjadi, *Langmuir*, **22**, 5597 (2006).
16. S. B. Campbell, T. Larson, N. M. B. Smeets, U. El-Jaby and T. F. L. McKenna, *Chem. Eng. J.*, **183**, 534 (2012).
17. P. Mondal, S. Ghosh, G. Das and S. Ray, *Chem. Eng. Process.*, **49**, 1051 (2010).
18. R. W. Luhning and H. Sawistowski., in *Proceedings of the International Solvent Extraction Conference*, J. G. Gregory, B. Evans and P. C. Weston, Eds., Society of Chemical Industry, London (1971).

19. J. Juswandi, M.S. Thesis, Oklahoma State University (1995).

20. L. Y. Yeo, O. K. Matar, E. S. Perez de Ortiz and G. F. Hewitt, *Chem. Eng. Sci.*, **57**, 1069 (2002).

21. L. Y. Yeo, O. K. Matar, E. S. Perez de Ortiz and G. F. Hewitt, *J. Colloid Interface Sci.*, **248**, 443 (2002).

22. M. Amouei, P. Khadiv-Parsi, M. M. Moosavian, N. Hedayat and A. A. Davoodi, *Iran. J. Chem. Chem. Eng.*, **5** (2008).

23. S. Kumar, K. S. Gandhi and R. Kumar, *Chem. Eng. Sci.*, **46**, 2363 (1991).

24. C. Tsouris and J. Dong, *Chem. Eng. Sci.*, **55**, 3571 (2000).

25. L. Y. Yeo, O. K. Matar, E. S. Perez de Ortiz and G. F. Hewitt, *Chem. Eng. Sci.*, **57**, 3505 (2002).

26. J. M. Lee and Y. Soong, *Ind. Eng. Chem. Process Des. Dev.*, **24**, 118 (1985).

27. B. P. Binks and T. S. Horozov, *Colloidal Particles at Liquid Interfaces*, B. P. Binks, T. S. Horozov Eds., Cambridge University Press, Cambridge (2006).

28. B. P. Binks and J. A. Rodrigues, *Langmuir*, **19**, 4905 (2003).

29. Y. Nonomura and N. Kobayashi, *J. Colloid Interface Sci.*, **330**, 463 (2009).

30. K. A. White, A. B. Schofield, P. Wormald, J. W. Tavacoli, B. P. Binks and P. S. Clegg, *J. Colloid Interface Sci.*, **359**, 126 (2011).

31. Z.-G. Cui, L.-L. Yang, Y.-Z. Cui and B. P. Binks, *Langmuir*, **26**(7), 4717 (2010).

32. I. Budai, O. Z. Nagy and G. Kaptay, *Colloids Surf. A- Physicochem. Eng. Asp.*, **377**, 325 (2011).

33. B. P. Binks, J. Philip and J. A. Rodrigues, *Langmuir*, **21**, 3296 (2005).

34. I. Akartuna, A. R Studart, E. Tervoort, U. T. Gonzenbach and L. J. Gauckler, *Langmuir*, **24**, 7161 (2008).

35. N. Yan, M. R. Gray and J. H. Masliyah, *J. Colloids Surf.*, **193**, 97 (2001).

36. S. Stiller, H. Gers-Barlag, M. Lergenmueller, F. Pflücker, J. Schulz, K. P. Wittern and R. Daniels, *J. Colloids Surf.*, **232**, 261 (2004).

37. J. Behin and S. Norouzi, *Pet. Coal*, **53**, 115 (2011).

38. B. P. Binks and S. O. Lumsdon, *Langmuir*, **16**, 3748 (2000).

39. A. Einstein, *Ann. Phys.*, **19**, 289 (1906).